111-textured BaTiO 3 ceramics elaborated by Templated Grain Growth using NaNbO 3 templates

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{111}-textured $BaTiO_3$ ceramics elaborated by Templated Grain Growth using $NaNbO_3$ templates

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Abstract
Highly textured {111} $BaTiO_3$ ceramics were obtained by templated grain growth using $NaNbO_3$ templates, with Lotgering factor F_{111}, around 95 %, one of the best values reported in the literature. Solid solution formation with $NaNbO_3$ templates changes the tetragonal structure into cubic, with paraelectric behaviour. The relative permittivity is lower than "pure" tetragonal $BaTiO_3$, but dielectric losses are improved with better thermal stability.

Keywords
Electroceramics, Texture, Templated Grain Growth, Tape casting

1. Introduction

Lead-free $BaTiO_3$ (BT) based perovskite materials present potential interest in numerous domains because of their dielectric, ferroelectric and piezoelectric properties. To improve the properties of such anisotropic materials, particular attention has been paid to textured microstructures in ceramic materials (i.e. grain orientation) [1, 2, 3]. Thus different texturation methods were developed: directional solidification technology [4], hot forging [2], Templated Grain Growth (TGG) [5, 6], Reactive Templated Grain Growth (RTGG) [6]... In order to orientate templates, different techniques were developed: slip casting, tape casting, extrusion centrifugal casting [7, 8]. These methods were reported for texturation of lead free materials, particularly for

$Na_{0.5}Bi_{0.5}TiO_3$-$BaTiO_3$ system [6, 9], but rarely for pure $BaTiO_3$. RTGG was successfully used for elaboration of {111} oriented $BaTiO_3$ ceramic [10], using reactive sintering between plate-like $Ba_6Ti_{17}O_{40}$ and $BaCO_3$ and for {110} oriented $BaTiO_3$ using needlelike TiO_2 particles [11]. However, dense ceramics are difficult to obtain due to decarbonatation during sintering (only 81 %) [12]. {111} textured $BaTiO_3$ ceramics were elaborated with plate-like $BaTiO_3$ templates and powder using TGG method, with relative density around 95 % of the theoretical one [13].

Nowadays, $NaNbO_3$ templates (NN) were successfully used for the texturation of alkaline niobate ceramics [14-16], but not for $BaTiO_3$. Thus, the aim of this work is (i) to obtain highly densified and highly textured $BaTiO_3$ ceramics by TGG process using $NaNbO_3$ templates and (ii) to investigate the structure and electrical properties of such anisotropic ceramics.

2. Experimental procedure

2.1. Synthesis of $NaNbO_3$ platelets and $BaTiO_3$ powders

$NaNbO_3$ platelets were synthesized using a process derived from the one previously reported [17]. $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ platelets (BNN5) were synthetized by Molten Salt Synthesis. Analytical grades $NaCO_3$, Bi_2O_3 and Nb_2O_5 were weighed in stoichiometric proportions, mixed with NaCl in anhydrous ethanol (oxide to salt weight ratio 1: 1.5) and heated at 1130 °C for 5 h in sealed alumina crucible. The remaining flux salt was then removed by washing several times with de-ionized water, until total removing of chloride ions. BNN5 platelets were then converted into $NaNbO_3$ templates by Topochemical Conversion (TC). This topotactic transformation preserves the initial morphology of BNN5 grains [17]. It corresponds to chemical reaction:

$$4\ Bi_{2.5}Na_{3.5}Nb_5O_{18} + 3\ Na_2CO_3 \rightarrow 20\ NaNbO_3 + 5\ Bi_2O_3 + 3\ CO_2.$$

BNN5 microcrystals were mixed with 10 % excess Na_2CO_3, according to stoichiometry of the reaction. NaCl was added as flux (oxide to salt weight ratio 1:1.5). The mixture was heated at 1000 °C for 6 h in sealed alumina crucible and then washed

several times using hot de-ionised water. The NN templates were separated using HCl (8 M), in order to dissolve Bi_2O_3 produced during TC reaction. Microstructures of BNN5 platelets and NN templates (fig. 1.a and b) consist of anisotropic platelets with 5-15 μm length and around 1μm thickness, close to those previously reported [17].

Equiaxial $BaTiO_3$ powder was obtained with low particle size 80 - 100 nm by solid state route at 900 °C. Splitting of the diffraction peaks (Fig. 2) confirms tetragonal structure: lattice parameters "a" = 0.4000 ± 0.0001 nm, "c" = 0.4022 ± 0.0002 nm, similar to reference values of tetragonal $BaTiO_3$ (a = 0.3994 nm, c = 0.4038 nm, JCPDS # 05-626).

2.2. Texturation of the ceramics by TGG

The tape casting slurry was prepared using non-aqueous formulation (volume ratio powder / templates 92:8) optimized in previous work [18] against organic way for reported results [10-13]. The large viscosity of the suspension (1 $Pa.s^{-1}$) and shearing stresses during casting led to the orientation of anisotropic NN templates in casting direction. The process includes the following steps: (i) first mixing of the suspension was performed 1h by using low rotation speed to avoid breaking templates, (ii) after adding binder + plasticizer, second mixing was performed by planetary milling at low rotation speed for 17 h, (iii) after degassing (24h), slurry was tape-casted onto a siliconed Mylar carrier film (doctor blade opening 600 μm, speed 2 $m.mn^{-1}$), (iv) tapes were dried at room temperature in a solvent saturated enclosure and (v) samples were cut and stacked by thermo-compression (50 °C - 60 MPa). The obtained pellets were then sintered using a two steps process: (i) carefully burning out of the organic additives (dispersant, binder and plasticizer) between 100 and 500°C (20°C/h) and (ii) sintering at 1150 °C for 10 h (200°C/h).

3. Results and discussion

As a matter of comparison with TGG process, a reference sample with the same powder: templates ratio was elaborated by conventional ceramic route without tape casting, using traditional uniaxial pressing. All samples were sintered at the same temperature.

Figure 2 presents XRD of $BaTiO_3$ powder, reference and textured samples, respectively. The splitting of (00l) peaks observed at 20° and 45° for powder are characteristic of tetragonal symmetry, while single peaks associated to cubic phase are observed for both reference and textured samples. The cubic symmetry obtained for both samples indicates that during sintering process, $BaTiO_3$ tetragonal phase was transformed into cubic one. This structure-modification can be attributed to the formation of a solid solution with $NaNbO_3$ templates, since same symmetry is obtained by conventional and TGG process. Indeed, structural refinement (Rietveld method, reference ceramic) led to Ti^{4+} / Nb^{5+} content around (87 ± 1) : (13 ± 1) mol% in B-site of the perovskite lattice. Similar behavior has been reported for Niobium-doped $BaTiO_3$ ceramics: above 0.8% Nb_2O_5 the structure changes from tetragonal to pseudo-cubic [19]. The calculated lattice parameter are "a" = 0.4001 ± 0.0002 nm for TGG ceramic and "a" = 0.4012 ± 0.0001 nm for reference ceramic respectively, close to those of cubic $BaTiO_3$ (a= 0.4031 nm, JCPDS # 031-0174).

X-ray diffraction pattern of TGG ceramic (surface of the sample parallel to casting direction), clearly shows major cubic perovskite phase and minor unidentified phase (fig. 2). The perovskite phase presents a strong (111) peak, characteristic of {111} preferential orientation, thus demonstrating efficiency of the texturation process. This result confirms that the tetragonal to cubic structure-modification can be attributed to the formation of a solid solution with $NaNbO_3$ templates while texturation is induced by orientation of templates by tape casting.

{111} texturation degree was evaluated around 95% using the Lotgering factor [20] by taking cubic $BaTiO_3$ as reference (JCPDS # 031-0174). This value is higher than 80% previously obtained by RTGG [10, 12] and 36% by TGG [13]. In the SEM micrography (fig.2c), the fractured sintered textured sample appears as well densified and exhibits a particular direction of grain growth, according with the high texturation degree.

Dielectric properties were measured from 100 Hz to 1 MHz using an impedance analyser. Variation of relative permittivity and dielectric loss versus temperature are presented in fig. 3. The measurements revealed linear decrease for $BaTiO_3$- 8% $NaNbO_3$ textured ceramic, compared with the well-known accident near 400 K for undoped $BaTiO_3$ ceramic associated to tetragonal-cubic phase transition at Curie temperature. Paraelectric behaviour observed for $BaTiO_3$- 8% $NaNbO_3$ textured ceramic is characteristic of non-ferroelectric material, in good agreement with cubic structure observed by XRD.

Curie-Weiss plot of ε^{-1} versus T clearly confirms the paraelectric behaviour for the $BaTiO_3$- 8% $NaNbO_3$ textured sample, with a change of slope around 408 K (fig.3 b). Calculations were performed using Curie-Weiss law, $\varepsilon^{-1} = (T-T_0) / C$, ε = relative permittivity, T = temperature (K), T_0 and C = Curie-Weiss temperature and constant. The results (table 1, T_0, C) are different from those obtained for "pure" $BaTiO_3$. This suggests that the anomaly can't be attributed to $BaTiO_3$ phase transition but likely comes from minor unidentified secondary phase. Finally, the dielectric losses are improved, (1-1.5%), and present good thermal stability, contrary to "pure" $BaTiO_3$.

Conclusion

Highly textured {111} $BaTiO_3$ ceramics were successfully elaborated by TGG method using $NaNbO_3$ templates. Optimization of the processing parameters allowed obtaining reproductively a high degree of {111} orientation with Lotgering factor, F_{111},

around 95 % (details about optimization will be published elsewhere). X-ray diffraction revealed a cubic structure, confirmed by the paraelectric behaviour of the textured ceramic. Finally, compared to "pure" $BaTiO_3$, the relative permittivity is slightly decreased but the dielectric losses are improved, with better thermal stability. Thus the most important results of this study are: (i) the very high degree of texturation, around 95%, one of the best values reported today in literature and (ii) the improvement of the dielectric losses with better thermal stability.

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	T_C (K)	T_0 (K)	C (K)
$BaTiO_3$ – 8% volume $NaNbO_3$ textured sample T > 408 K	/	94 ± 5	233167 ± 3400
$BaTiO_3$ – 8% volume $NaNbO_3$ textured sample T < 408 K	/	243 ±5	122440 ± 5900
Undoped $BaTiO_3$	400 ± 5	370 ± 5	138500 ± 5600

Table 1: Calculated values for the Curie-Weiss plot of fig. 3.b (1 MHz)

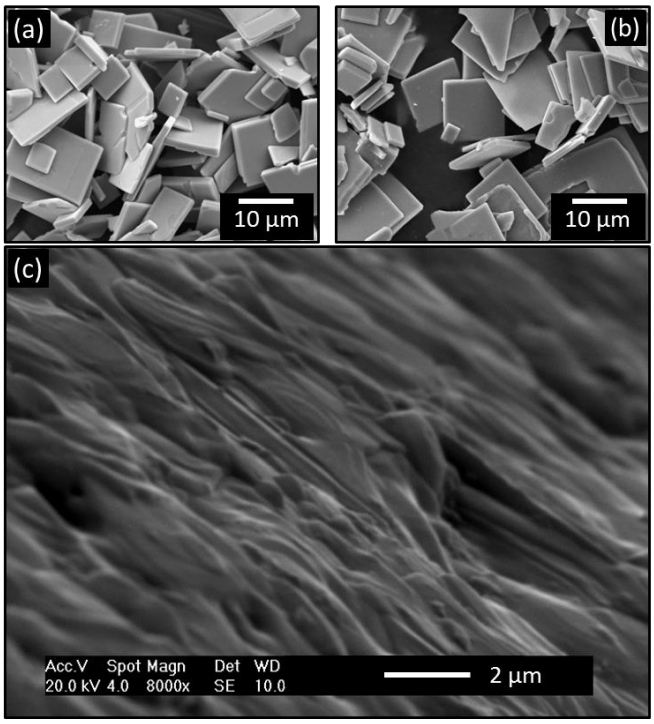

Fig. 1: SEM picture of (a) $Bi_{2.5}Na_{3.5}Nb_5O_{18}$ platelets obtained by Molten Salts Synthesis, (b) $NaNbO_3$ templates obtained by Topochemical Conversion (c) $BaTiO_3$ – 8% volume $NaNbO_3$ textured sample (fracture).

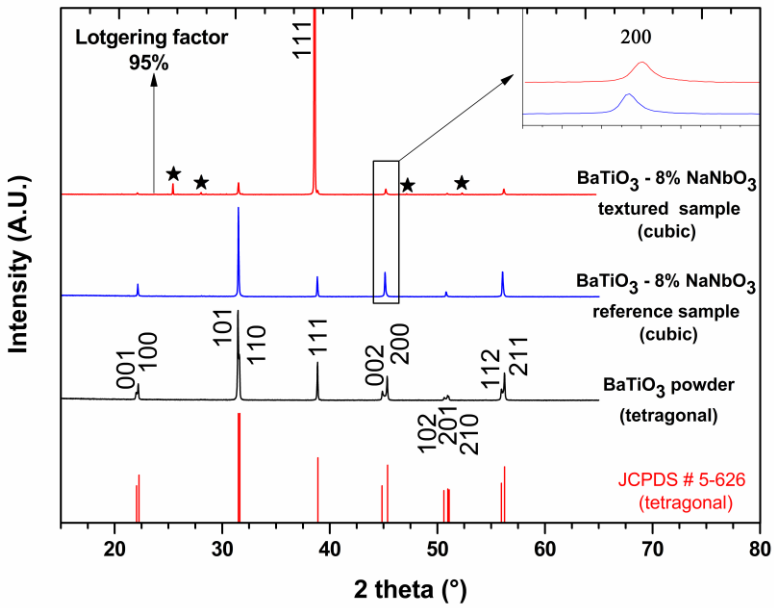

Fig. 2: X-ray diffraction patterns (θ/2θ, Cu $K\alpha_1$, color online): $BaTiO_3$ – 8% volume $NaNbO_3$ textured sample (stars = unidentified secondary phase), $BaTiO_3$ – 8% volume $NaNbO_3$ reference sample, tetragonal "pure" $BaTiO_3$ powder. Insert = detail showing the lack of splitting for (200) peak (the scale is different).

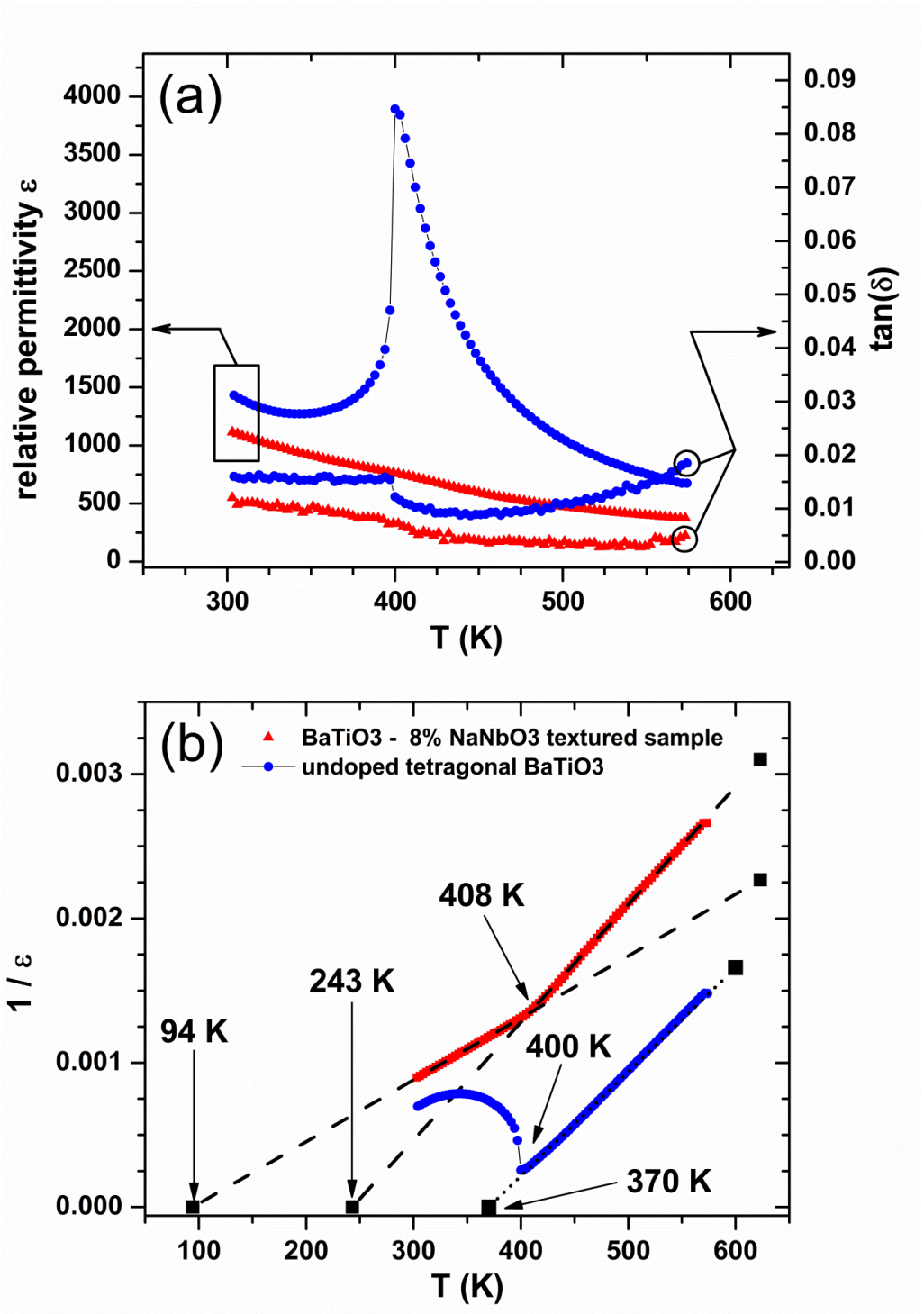

Fig. 3: $BaTiO_3$ – 8% volume $NaNbO_3$ textured sample and tetragonal "pure" $BaTiO_3$ ceramic (color online): (a) relative permittivity and dielectric losses versus temperature (1 MHz), (b) reciprocal relative permittivity versus temperature (Curie-Weiss law, 1 MHz).